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Synthesis of 4-,5-, and 6-Boron Metallocarboranes
from the Polyhedral $C_2B_5H_7$ System

Vernon R. Miller and Russell N. Grimes
Department of Chemistry
University of Virginia
Charlottesville, Virginia 22901

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13. ABSTRACT A series of more than 20 new cobalt(III)-small carborane sandwich complexes, of which six are described in this paper, has been prepared from <u>closo-$C_2B_5H_7$</u> via reduction with sodium naphthalide in THF, followed by reaction with $CoCl_2$ and NaC_5H_5 and air oxidation. Separation on silica gel columns and TLC plates has given $(\pi-C_2B_4H_6)Co(\eta-C_5H_5)$, $(\pi-C_2B_5H_7)Co(\eta-C_5H_5)$, $(\pi-C_2B_6H_8)Co(\eta-C_5H_5)$, $(\pi-C_2B_4H_6)Co_2(\eta-C_5H_5)_2$, $(\pi-C_2B_5H_7)Co_2(\eta-C_5H_5)_2$ and $(\pi-C_2B_6H_8)Co_2(\eta-C_5H_5)_2$, all of which are air-stable sublimable solids. The characterization is based on boron-11 and proton nmr, infrared, and mass spectra.			

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Sandwich complex						
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Carboranes						

Synthesis of 4-,5-, and 6-Boron Metallocarboranes
from the Polyhedral $C_2B_5H_7$ System

Vernon R. Miller and Russell N. Grimes*
Department of Chemistry
University of Virginia
Charlottesville Virginia 22901

Abstract

A series of more than 20 new cobalt(III)-small carborane sandwich complexes, of which six are described in this paper, has been prepared from closo- $C_2B_5H_7$ via reduction with sodium naphthalide in THF, followed by reaction with $CoCl_2$ and NaC_5H_5 and air oxidation. Separation on silica gel columns and TLC plates has given $(\pi-C_2B_4H_6)Co(\pi-C_5H_5)$, $(\pi-C_2B_5H_7)Co(\pi-C_5H_5)$, $(\pi-C_2B_6H_8)Co(\pi-C_5H_5)$, $(\pi-C_2B_4H_6)Co_2(\pi-C_5H_5)_2$, $(\pi-C_2B_5H_7)Co_2(\pi-C_5H_5)_2$, and $(\pi-C_2B_6H_8)Co_2(\pi-C_5H_5)_2$, all of which are air-stable sublimable solids. The characterization is based on boron-11 and proton nmr, infrared, and mass spectra.

Sir:

The two-electron alkali metal reduction of closed polyhedral carboranes to yield open-faced dianions which are capable of metallocene-like π -coordination to transition metal ions, has been established by Hawthorne and co-workers as a general reaction for closo-carboranes having six, eight, or ten boron atoms.¹⁻³ We anticipated that similar treatment of closo- $C_2B_5H_7$ would yield an open-faced $C_2B_5H_7^{2-}$ species, from which complexes such as $(\pi-C_2B_5H_7)Co(\pi-C_5H_5)$ could be prepared. In fact, the reduction of $C_2B_5H_7$ and subsequent reactions with metal ions have given an unexpectedly complex chemistry, and have generated a wealth of air-stable metallocarboranes in which several structural families are represented. We report here the overall reaction scheme and several complexes which are representative of two of the structural classes identified thus far, $(C_2B_nH_{n+2})Co(C_5H_5)$ and $(C_2B_nH_{n+2})Co_2(C_5H_5)_2$ ($n = 4-6$).

The reaction of $C_2B_5H_7$ with two mol equivalents of sodium naphthalide at 25° in tetrahydrofuran (THF) proceeds without evolution of H_2 or other volatiles, yielding a dark orange solution presumed to contain the disodium salt of the previously unknown $C_2B_5H_7^{2-}$ ion. The reaction of this product with anhydrous $CoCl_2$ and NaC_5H_5 in THF under N_2 takes place readily at 25° to give a dark brown solution. Subsequent evaporation of most of the THF, treatment with water and acetone, and exposure to air followed by separation of the products via column and thin-layer chromatography on silica gel, has disclosed well over 20 carborane-metal-

cyclopentadienide complexes. All of those characterized thus far are electrically neutral species containing one to three cobalt atoms in the formal +3 state. The major product, a yellow solid obtained in 20-25% yield, has been characterized as $(\pi\text{-C}_2\text{B}_4\text{H}_6)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (I). Formed in much smaller yields are the additional monocobalt species $(\pi\text{-C}_2\text{B}_5\text{H}_7)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (II, orange) and $(\pi\text{-C}_2\text{B}_6\text{H}_8)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (III, red), and the dicobalt species $(\pi\text{-C}_2\text{B}_4\text{H}_6)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (IV, red), $(\pi\text{-C}_2\text{B}_5\text{H}_7)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (V, red-brown), and $(\pi\text{-C}_2\text{B}_6\text{H}_8)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (VI, red-brown). All six compounds are air-stable sublimable solids.

Compounds I-VI all exhibit strong mass spectroscopic parent peaks, and in each case the intensities in the parent region are in close agreement with the calculated composition based on known isotopic distributions. In addition, the elemental compositions of I, III, IV, V, and VI have been confirmed by exact mass determinations on a high resolution spectrometer. The mass spectrum of each compound contains an intense peak at m/e 124 corresponding to $^{59}\text{Co}^{12}\text{C}_5\text{H}_5^+$, and the dicobalt complexes also exhibit a very strong peak at m/e 189 corresponding to $^{59}\text{Co}(\text{C}_5\text{H}_5)_2^+$, a characteristic feature of the spectra of compounds containing more than one metal-cyclopentadienide moiety.⁴ The infrared spectra of I-VI exhibit B-H stretching bands as well as absorptions attributed to cyclopentadienide and carboranyl C-H groups.

The nmr data presented in Tables I and II are consistent with the geometries in Figure 1, but alternative isomeric structures cannot be ruled out at this stage (the suggested structures are based on idealized

polyhedra having 7 to 10 vertices and are analogous to isoelectronic carboranes and metallocarboranes whose structures are known from X-ray studies⁵). Discussion of the nmr spectra will be deferred to a later report, except to note that all of the compounds other than I exhibit a doublet at very low field (-57 to -118 ppm) which we assign to 4-coordinate apical BH groups adjacent to the metal. This particular structural feature has not been previously described in metallocarborane chemistry. The extremely low-field doublet at δ -118 in the spectrum of V is assigned to a unique 4-coordinate BH adjacent to two cobalt atoms (Figure 1, V).

Complex VI is evidently a new structural isomer of the $(C_2B_8H_8)Co_2(C_5H_5)_2$ species described earlier¹, while I and III are analogs of the known $(C_2B_4H_6)Fe(CO)_3$ ⁶, $(C_2B_4H_6)Fe(C_5H_5)$ ⁷, and $(C_2B_8H_8)Mn(CO)_3$ ⁸ species, respectively. The formal $C_2B_5H_7^{2-}$, $C_2B_4H_6^{4-}$, and $C_2B_5H_7^{4-}$ ligands in II, IV, and V, respectively, have not been previously reported.

Other complexes obtained in this reaction system include $(C_2B_3H_5)Co_2(C_5H_5)_2$, $(C_2B_5H_7)Co_3(C_5H_5)_3$, and a family of biscarborane species such as $[\pi-(\sigma-C_2B_5H_6)-C_2B_4H_5]Co(\pi-C_5H_5)$.⁹ Investigation of the reaction and its metallocarborane products is continuing.

Acknowledgment

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Table I

32.1-MHz ^{11}B nmr Chemical Shifts and Coupling Constants

<u>Complex</u>	<u>δ, ppm(J, Hz)^a</u>	<u>Area Ratio</u>
I	-6.7(166); -1.4 (170)	3:1
II	-56.5(174); -11.3(146); +1.3 (166); +10.7(162); +21.0(179)	1:1:1:1:1
III	-66.3(150); -4.3(173); +3.5(185); +9.0(168); +15.6(141); +20.4(162)	1:1:1:1:1:1
IV ^b	-57.2(157)	
V	-118.8(162); -3.7(169); +12.6(163)	1:2:2
VI	-81(143); +3.4(147); +5.9(141); +15 (~150)	1:2:2:1

^aChemical shifts in ppm relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)$. All spectra were obtained in CCl_4 solution. ^bHigh-field resonances are not clearly distinguishable due to the presence of complex V in the sample.

Table II

100-MHz ^1H Nmr Data

		δ , ppm ^a	
<u>Complex</u>	<u>C₅H₅</u>	<u>Carborane</u> <u>C-H</u>	<u>Area Ratio</u>
I	-4.86	-3.90	5:2
II	-4.92	-4.42 -3.97	5:1:1
III	-4.99	-5.88 -3.81	5:1:1
IV	-4.54	b	
V	-4.81	-3.88	10:2
VI	-4.88	-4.68 -4.44	10:1:1

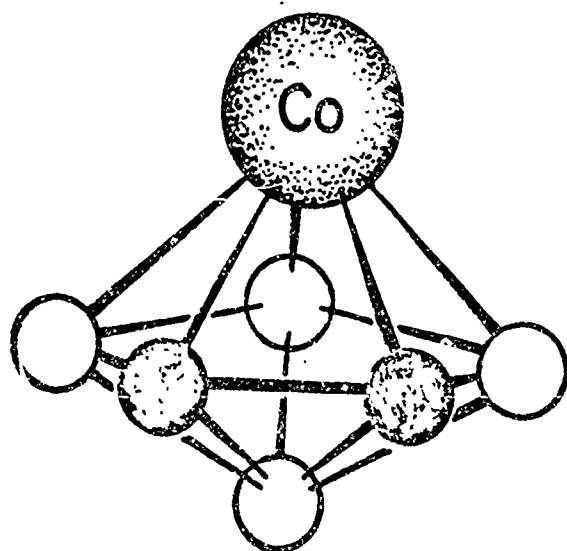
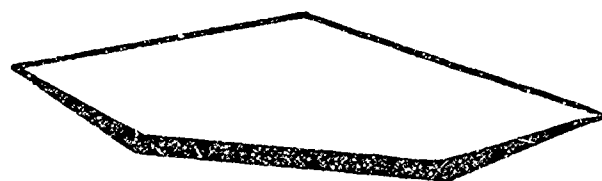
^aChemical shifts relative to $(\text{CH}_3)_4\text{Si}$; all spectra were obtained in CCl_4 solution. The expected H-B quartets are not well resolved and are largely masked by the H-C peaks. ^bToo weak to be clearly observed.

References

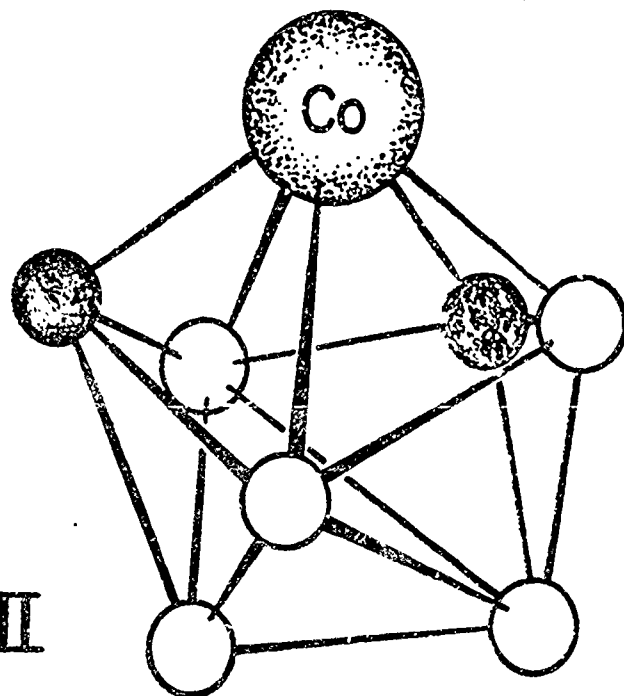
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Figure Caption

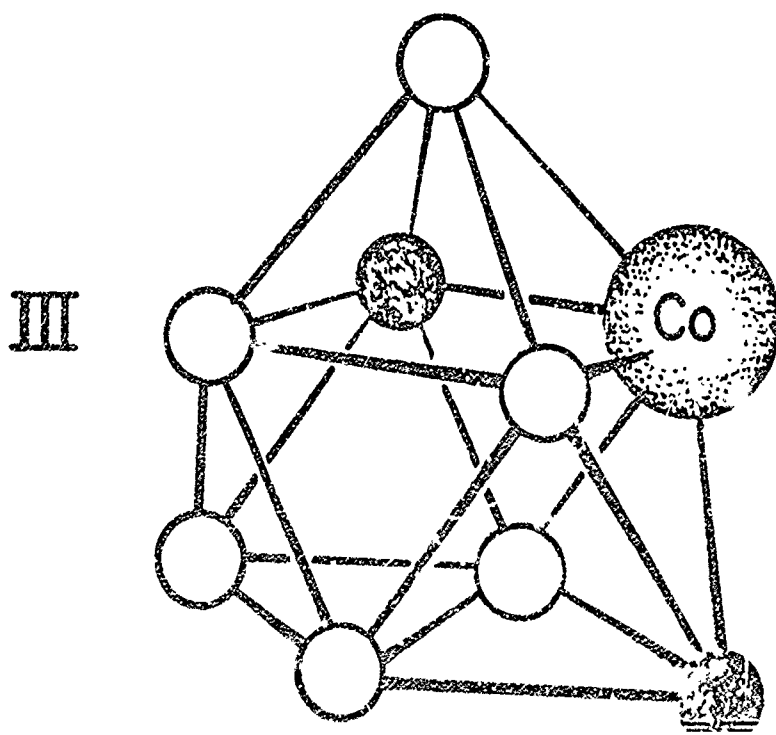
Figure 1. Possible structures for $(\pi\text{-C}_2\text{B}_4\text{H}_6)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (I),
 $(\pi\text{-C}_2\text{B}_5\text{H}_7)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (II), $(\pi\text{-C}_2\text{B}_6\text{H}_8)\text{Co}(\pi\text{-C}_5\text{H}_5)$ (III),
 $(\pi\text{-C}_2\text{B}_4\text{H}_6)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (IV), $(\pi\text{-C}_2\text{B}_5\text{H}_7)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (V), and
 $(\pi\text{-C}_2\text{B}_6\text{H}_8)\text{Co}_2(\pi\text{-C}_5\text{H}_5)_2$ (VI). Solid circles represent CH
groups, and open circles BH groups.



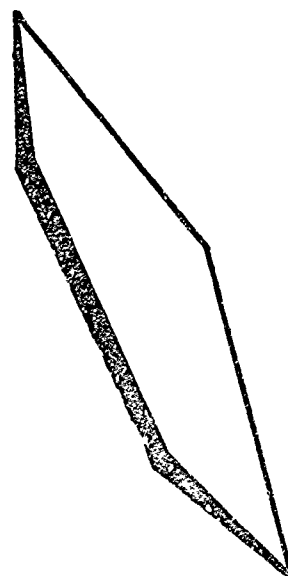
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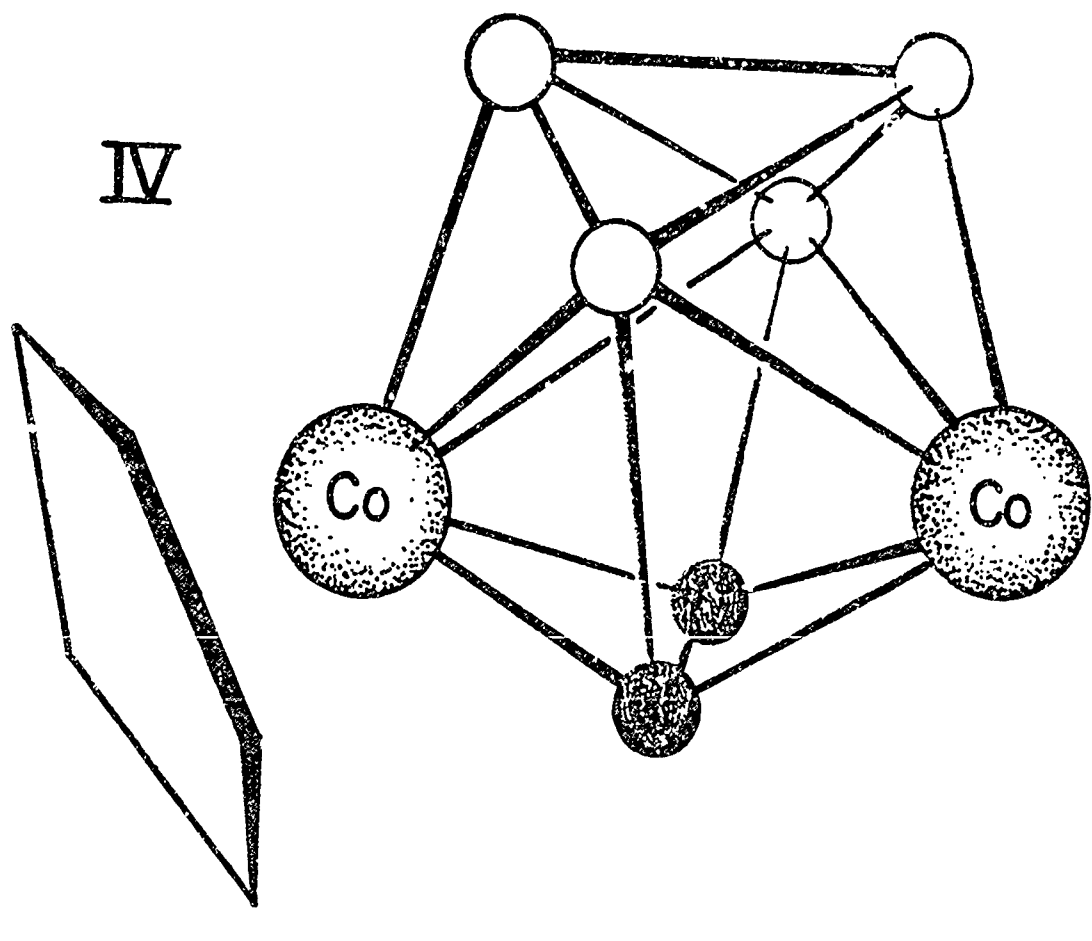
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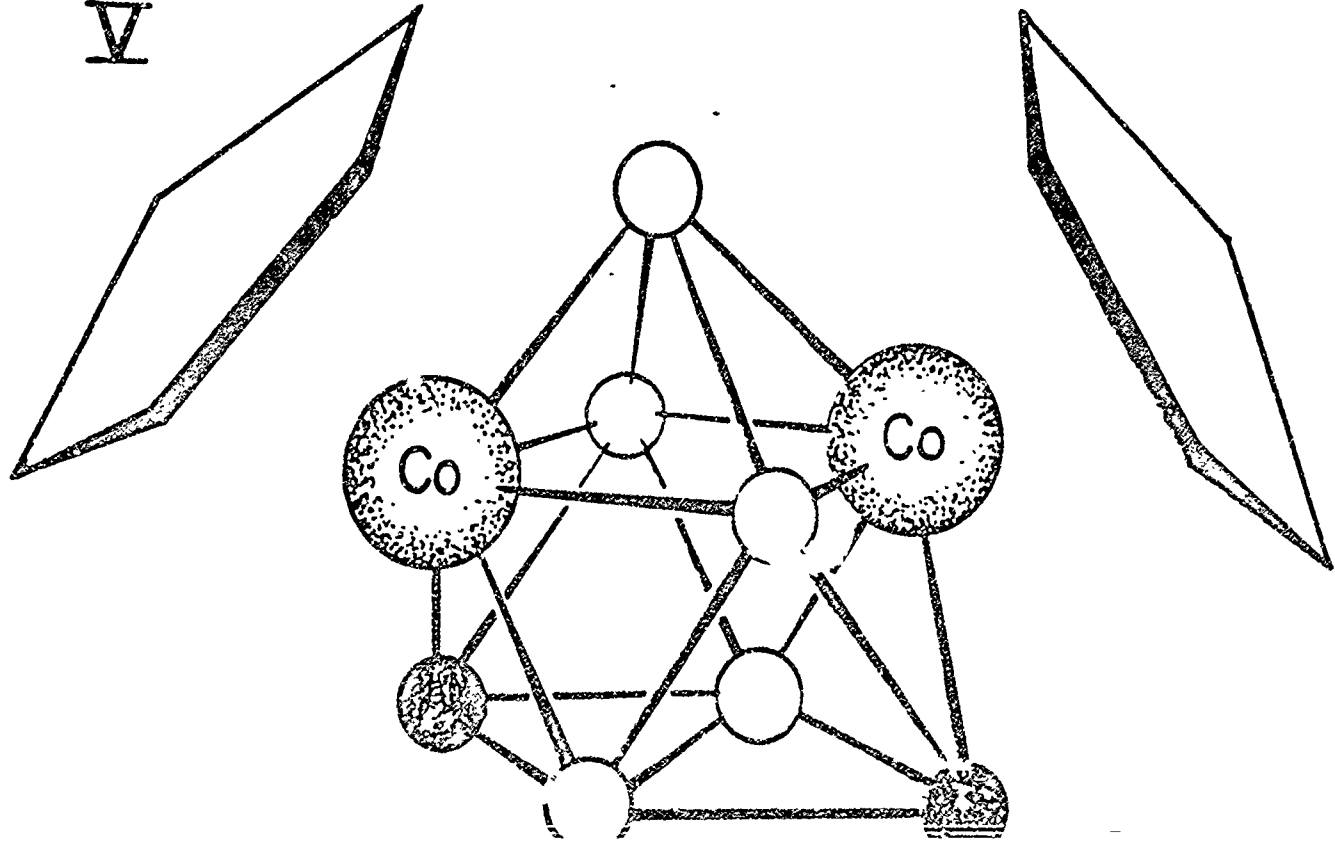
III

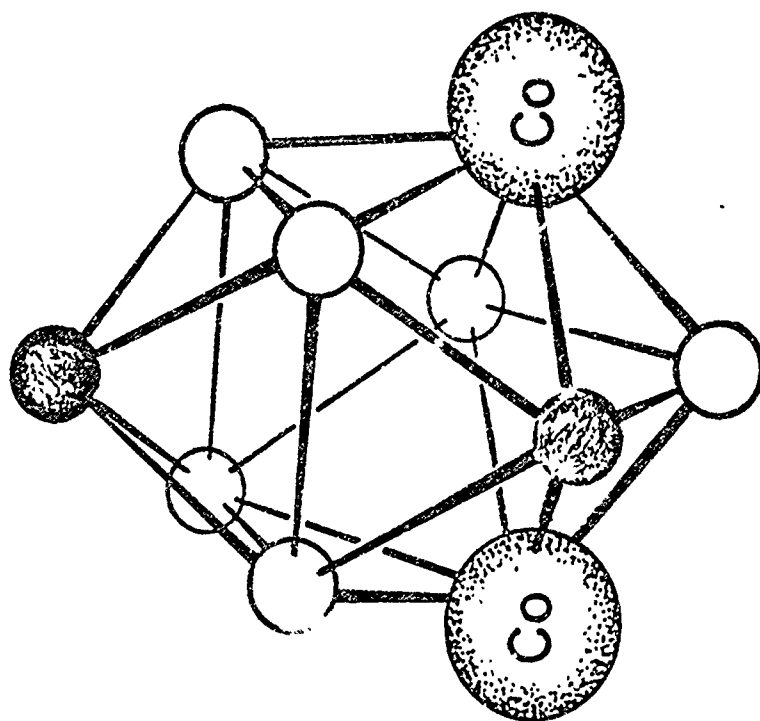


IV



V





VI